



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 8/32, 224/00, C08L 37/00	A1	(11) International Publication Number: WO 97/23516 (43) International Publication Date: 3 July 1997 (03:07:97)
(21) International Application Number: PCT/US96/20735 (22) International Filing Date: 20 December 1996 (20.12.96) (30) Priority Data: 08/576,948 22 December 1995 (22.12.95) US (71) Applicant: THE VALSPAR CORPORATION [US/US]; 1101 Third Street South, Minneapolis, MN 55415 (US). (72) Inventors: YANG, Lucy; Apartment 8, 1634 W. County Road B., Roseville, MN 55113 (US). TOBIAS, Michael, A.; 2880 Jewel Lane North, Plymouth, MN 55447 (US). RUHOFF, Philip, J.; 5344 James Avenue South, Minneapolis, MN 55419 (US). HUNG, Robert; 628 McFaddens Trail, Eagan, MN 55123 (US). STENSON, Paul; 18825 - 34th Avenue North, Plymouth, MN 55447 (US). (74) Agent: BRUESS, Steven, C.; Merchant, Gould, Smith, Edell, Welter & Schmidt, 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402-4131 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: AQUEOUS CROSS-LINKABLE COATING COMPOSITION		
(57) Abstract <p>An aqueous cross-linkable coating composition, which includes a polymer system capable of being cross-linked by a process which includes the reaction of a cyclic carbonate group with an amine group, is provided. A polymer having cyclic carbonate groups and amine groups or amine precursor groups, a method of preparing the polymer and a coated substrate formed from the aqueous cross-linkable coating composition are also provided.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

AQUEOUS CROSSLINKABLE COATING COMPOSITION

BACKGROUND OF THE INVENTION

The formation of polymeric film coatings on a variety of substrates, usually for protective or adhesive purposes, has been extensively studied. The enhancement of the performance characteristics of such coatings by crosslinking the components of the composition during and/or after film formation from a coating composition is also a well established technology. A variety of approaches have been developed to carry out the crosslinking ("cure") step under low temperature conditions. A large number of the low temperature curable coating compositions are, however, solvent-based compositions which may present potential hazards in terms of flammability and toxicity. For many applications it would be very desirable to be able to employ aqueous-based coating compositions which could be coated onto a substrate and cured at low temperatures (e.g., at ambient temperatures). Preferably, the chemical reactions used to crosslink such aqueous-based coating compositions would not rely on reactive functional groups such as aziridines or isocyanates which have often been linked to toxicity problems.

In response to the need for low temperature curable aqueous coating systems, a great number of aqueous-based coatings, typically containing lattices of film-forming polymers, have been developed. The polymeric lattices are usually produced via aqueous emulsion polymerization of ethylenically unsaturated monomers. The properties of the coatings produced from these aqueous lattices are typically improved by incorporating some capacity into the composition which allows the polymer film to be crosslinked after application to a substrate. This cure capacity may be achieved by introducing a crosslinking agent as a second component into the coating composition. An alternative approach is to render the coating composition self-crosslinkable through the inclusion of appropriate functional groups in the polymer system. Unfortunately the curing reaction required to produce a crosslinked film using many of these coating systems which have been developed must be carried out at elevated temperatures, e.g., by baking the coated substrate in an oven.

A variety of aqueous-based coating systems have been developed which permit the curing process to be carried out at ambient temperatures. Among the products of this type are aqueous coating systems which include amine-containing polymers blended with non-polymeric ketone-containing compounds such as acetoacetates or

acetoacetamides. Related aqueous coating systems which include vinyl polymer(s) bearing chain-pendant amine and/or carbonyl functional groups in either the same or different polymer molecules have also been reported. Other systems are based on combinations of polymers having epoxy reactive groups (e.g., amino groups or hydroxyl groups) with a polyepoxide compound and a metal chelate epoxy-cure catalyst. Yet another ambient curing coating composition has been developed using an aqueous dispersion of acrylic polymers which contain pendant acetoacetoxy, glycidyl and carboxylic acid groups.

Another aqueous-based, film-forming crosslinkable coating composition has been developed based on an aqueous dispersion of autoxidisable copolymers having residual unsaturation, such as the polymers derived from polymerizations of monomer mixtures which include a low reactivity multi-functional comonomer having an autoxidizable group (e.g., allyl esters of α,β -unsaturated mono- and dicarboxylic acids).

The autoxidizable self-crosslinkable polymer systems typically require the inclusion of an autoxidation catalyst, such as a drier salt, in order to achieve suitable curing rates.

One of the most effective methods of generating a highly crosslinked polymer film from an aqueous self-crosslinkable coating composition is based on the reaction of a carboxylic acid functional waterborne acrylic latex with a multifunctional aziridine material. Unfortunately, systems based on this crosslinking chemistry are generally sold as two-package systems since the shelf life of compositions containing both the carboxylic acid functional latex and the multifunctional aziridine is extremely short. In addition, multifunctional aziridine materials are quite toxic and present handling, storage and exposure issues.

The available methods of producing crosslinkable aqueous coating compositions have certain disadvantages in terms of toxicity, cost, inferior performance, difficulty in developing modifications and the like. Accordingly, a continuing need exists for the development of new low temperature aqueous-based, crosslinkable polymeric coating compositions.

SUMMARY OF THE INVENTION

The present invention provides an aqueous crosslinkable coating composition which includes a polymer system capable of being crosslinked by a process which includes the reaction of a cyclic carbonate group with an amine group. The polymer

system includes a polymer bearing cyclic carbonate functional groups and/or amine or amine precursor functional groups. When a coating is formed from the composition, the polymer becomes crosslinked during and/or after film formation primarily through the reaction of the cyclic carbonate groups with the amine groups.

5 The reactive groups which are involved in the crosslinking reaction may be present in the polymer system in a number of configurations. In one embodiment of the invention, the polymer system includes a polymer having both cyclic carbonate functional groups and amine or amine precursor functional groups. The present coating composition may also be based on an aqueous dispersion of a polymer system which
10 includes a first polymer bearing cyclic carbonate functional groups and a second polymer bearing amine or amine precursor functional groups.

DETAILED DESCRIPTION OF THE INVENTION

15 The present crosslinkable coating composition includes an aqueous dispersion of a polymer system which includes cyclic carbonate functional groups and amine or amine precursor functional groups. As indicated supra, the polymer system may or may not include both cyclic carbonate groups and amine groups (or precursors thereof) in the same molecular entity.

20 As used herein, an "aqueous dispersion" includes a polymer component present as a separate phase in an aqueous carrier medium of which water is the principal component. Typically at least about 55 wt.% and preferably at least about 70 wt.% of the carrier medium is water. Minor amounts of organic liquid(s) may be present in the carrier medium if desired or required. Typically, the waterborne polymer component will be in the form of an aqueous latex, e.g., an aqueous dispersion of a vinyl addition
25 polymer produced via emulsion polymerization. Other examples of suitable aqueous dispersions include compositions prepared by dispersing a carboxylate group-containing polymer in an aqueous carrier medium. The carboxylate group-containing polymer may be prepared in an organic solvent and then dispersed in an aqueous carrier medium containing a base. Another method suitable for preparing the present aqueous
30 dispersion includes dispersing a solid carboxylic acid-containing polymer in an aqueous solution having a basic pH. As used herein, the term "carboxylate group" includes both carboxylic acid groups and salts thereof. Typically, the carboxylate group-containing

polymer includes carboxylic acid groups present as a water soluble salt. Suitable dispersable polymers which may be used to form the present aqueous dispersion include polyurethane polymers bearing carboxylate groups and/or nonionic groups (such as polyoxyethylene groups) which render the polyurethane more water-dispersible.

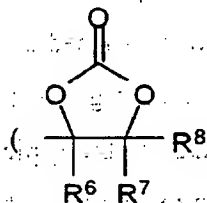
5 The present aqueous crosslinkable coating compositions possess good storage stability and are capable of being cured (crosslinked) to provide film coatings having excellent performance properties. In particular, coatings formed from the present composition exhibit good durability, toughness, solvent and water resistance and are typically tack-free. The present compositions may also be used to prepare coatings
10 which exhibit excellent mar and abrasion resistance. Moreover, due to the nature of the functional groups involved in the crosslinking reaction, the present compositions are typically characterized by relatively low toxicity and thus present less handling and storage problems than many commercial systems used in similar applications.

 Crosslinking of the present aqueous-based compositions may often occur
15 effectively at ambient or low temperatures (e.g. up to 50° C. or 60° C., and often within the range of 15° to 25° C., which is taken as the typical range for ambient temperature), although higher crosslinking temperatures may also be used if desired (no upper limit is intended). Drying (i.e. allowing or causing the aqueous-based carrier medium to become removed) before or concurrent with the crosslinking process may also usually
20 be effected at or close to ambient temperature. A substrate is typically coated using the present coating composition by applying the composition to the substrate, drying at ambient temperature and aging the resulting film at ambient temperature to develop crosslinking in the coating.

 The ratio of amine groups to cyclic carbonate groups present in the polymer
25 system is typically within the range of about 50:1 to 1:50, preferably about 25:1 to 1:25 and, most preferably about 10:1 to 1:10. The present polymer system typically includes an amount of amine groups within the range of about 5 to about 150 millimoles per 100 g of polymer solids and an amount of cyclic carbonate groups within the range of about 5 to 150 millimoles per 100 g of polymer solids. Polymers bearing cyclic carbonate
30 groups generally include about 0.1 to about 40 and, preferably, about 1 to about 20 mole% polymerized units bearing cyclic carbonate groups. Similarly, polymers bearing amine groups typically include about 0.1 to about 40 and, preferably, about 1 to about

20 mole% polymerized units bearing amine groups. As indicated herein, some or all of the amine groups may be present in protected form, i.e., as amine precursor groups. As described herein, the cyclic carbonate groups and amine groups may be present on different polymer chains (different molecular entities). In a preferred embodiment, both types of reactive functional groups may be present on the same polymer chain (same molecular entity).

The cyclic carbonate groups included in the present polymer system are typically in the form of a five-membered ring cyclic carbonate group or a six-membered ring cyclic carbonate group. Preferably, the present coating composition includes a polymer having pendant five-membered ring cyclic carbonate group(s). In a preferred embodiment, the polymer includes a relatively unhindered five-membered ring cyclic carbonate group, such as a cyclic carbonate functional group having the formula:



where R^6 , R^7 and R^8 are independently chosen from hydrogen, alkyl, benzyl and aryl (e.g., phenyl). The alkyl, benzyl or aryl groups may optionally be substituted with one or more substituents such as $\text{C}_1\text{-C}_3$ alkyl, halogen, cyano, hydroxy, $\text{C}_1\text{-C}_3$ alkoxy or alkylsulfonyl. Preferably, R^6 , R^7 and R^8 are each independently hydrogen or lower alkyl ($\text{C}_1\text{-C}_6$ alkyl).

The portion of the polymer system which is capable of reacting with the cyclic carbonate groups includes amine groups and/or amine precursor groups. The amine groups (or amine precursor groups) may be covalently bonded to a polymer, e.g., as chain-pendant amine groups.

A variety of amine groups may be employed in the present polymer systems. As used herein, the term "amine groups" includes functional groups which include a basic nitrogen atom capable of reacting with the carbonyl carbon of a carbonate group to form an $(\text{H})\text{N-C}(\text{O})$ bond. Thus, suitable amine groups include hydrazines, semicarbazides, hydroxylamines, alicyclic amines and aliphatic amines. The amine groups include

primary and/or secondary amine groups. One example of a suitable amine group is an aminoalkyl carboxylate group of the formula $-C(O)-O-R^1-NH_2$, where R^1 is an alkylene group having from 2 to 20 carbon atoms. Another example of an amine group which is particularly suitable for use in the present polymer system is an aminoalkyl carboxylate group of the formula $-C(O)-O-R^2-(NH-R^2)_m-NH_2$, where R^2 is an ethylene or substituted ethylene group and m is typically an integer from 0 to about 4. Preferably, R^2 is $-CH_2CH_2-$, $-CH(CH_3)CH_2-$ or $-CH_2CH(CH_3)-$.

In order for the crosslinking reaction to occur, the present coating composition need only include groups which are capable of being converted into an amine group, e.g., under either manufacturing or curing conditions (i.e., an "amine precursor group").

As long as a polymer system is capable of containing primary or secondary amine groups at the time the curing reaction with the cyclic carbonate groups occurs, the polymer system is suitable for use in the present coating compositions. Thus the present polymer system may include a polymer bearing amine precursor groups. Examples of suitable amine precursor groups include oxazolines, ketimines and isocyanates. These types of functional groups may be converted into a free amine group on contact with water under appropriate conditions.

Polymers bearing amine precursor groups may be prepared by a variety of methods. An amine group bearing polymer may be prepared in an organic solvent using methods such as are described herein. The amine groups may then be reacted with an appropriate reagent to convert all or a portion of the amine groups into oxazoline groups or ketimine groups. Alternatively, a vinyl addition polymer containing amine precursor groups may be prepared by reacting a monomer mixture which includes an ethylenically unsaturated amine precursor monomer. In one such method, the amine precursor groups may be oxazoline groups derived from the polymerization of an ethylenically unsaturated oxazoline monomer (e.g., an oxazoline having an unsaturated substituent in the 2-position). An example of a suitable unsaturated oxazoline monomer would be 2-isopropenyl oxazoline. Hydrolysis of oxazoline groups in the precursor polymer will yield aminoalkyl ester groups and hence provide chain-pendant amine groups.

In another such method, the amine precursor groups may include ketimine groups derived from the polymerization of a ketimine unsaturated monomer. Such monomers may be produced by first reacting a ketone or aldehyde with an aliphatic

amino compound (selected from primary amines, secondary amines, and ethanolamines) to produce a ketimine, and further reacting the ketimine with an ethylenic derivative containing an ethylenically unsaturated group. A ketimine monomer may also be prepared by reacting an amine-containing ethylenically unsaturated monomer with a ketone or aldehyde (see e.g., U.S. Pat. 4,328,144). Hydrolysis of ketimine groups ("amine precursor") in the polymer would generate chain-pendant amine functional groups.

The present polymer system includes a polymer having cyclic carbonate groups and/or amine or amine precursor groups and preferably having an weight average molecular weight within the range of about 5,000 to about 6,000,000 and more preferably about 30,000 to about 2,000,000. For example, the polymer may include a vinyl addition polymer produced via an emulsion polymerization process. Vinyl addition polymers prepared by this process typically have molecular weights of at least about 100,000 and often have molecular weights which range up to about 2,000,000 or higher. Polyurethane-based polymer systems including polyurethanes typically having molecular weights ranging from about 5,000 to about 200,000 may also be employed in the present coating compositions.

By a "vinyl addition polymer" in this specification is meant any addition polymer derived from one or more ethylenically unsaturated monomers, i.e., the term is intended to be used in a general sense (and is not merely directed to polymers derived from monomers having the vinyl grouping) and embraces such polymers as acrylic polymers and polymers comprising a high proportion of polymerized vinylidene chloride, vinyl acetate, vinyl chloride, styrene and/or a-methylstyrene units.

The vinyl addition polymer may be formed from ethylenically unsaturated monomer(s) by standard polymerization techniques. For example, a vinyl addition polymer for use as the polymer component of the present compositions may be prepared by any suitable free-radical initiated polymerization technique, a free-radical initiator and (usually) appropriate heating being employed. The polymerization is normally effected in an aqueous medium and, in particular, aqueous emulsion polymerization may be used to prepare an aqueous latex of the polymer with conventional dispersants and initiators being used (e.g. anionic and/or non-ionic emulsifiers such as sodium salts of dialkylsulphosuccinates, sodium salts of sulphated oils, sodium salts of alkyl sulfonic

acids, sodium, potassium and ammonium alkyl sulfates, C₂₂₋₂₄ fatty alcohols, ethoxylated fatty acids and/or fatty amides, and sodium salts of fatty acids such as sodium stearate and sodium oleate; the amount used is usually 0.1 to 3% by weight on the weight of total monomer(s) charged and conventional free radical initiators being used (e.g. hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate). Redox initiator systems, such as t-butyl hydroperoxide/isoascorbic acid, may also be used. The amount of initiator is generally 0.05 to 3% based on the weight of total monomers charged.

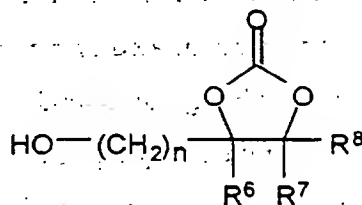
A latex resulting from the formation of a vinyl addition polymer via emulsion polymerization could be used "as is" in the composition (apart from optional dilution or concentration or the addition of coalescing solvent to assist in film formation). Alternatively, the latex may be blended with a second latex. For example, a latex containing a polymer bearing cyclic carbonate functional groups may be blended with a second latex which includes a polymer bearing amine or amine precursor functional groups. The present coating composition may also be based on a carboxylic acid-containing polymer prepared in an organic solvent which is then dispersed in water in the presence of a base, such as ammonia or an amine, to produce an aqueous dispersion (water-reducible system). Other aqueous polymer systems derived from solid (dry) polymers containing carboxylic acid groups which are dispersed (dissolved) in water containing a base may also be employed in the present compositions.

As mentioned supra, polymers other than vinyl addition polymers may also be used as a polymeric component of the aqueous dispersion. For example, a polyurethane polymer bearing carboxylic acid groups (e.g. laterally disposed) may be employed. As is well known, polyurethane polymers (or analogous polymers such as polyureas) may be produced by reacting an organic polyisocyanate with an organic compound containing at least two isocyanate-reactive groups, such as a macropolyol with the optional inclusion of a low molecular weight polyol. A favored route to their formation involves the formation of an isocyanate-terminated prepolymer followed by chain extension with an active hydrogen containing compound. A polyurethane bearing carboxylic acid groups could be made by employing as a reactant, in the polyurethane prepolymer formation step, an isocyanate-reactive compound having at least one carboxylic acid group and at least two isocyanate reactive groups (such as 2,2-

dimethylolpropionic acid), together with other compound(s) bearing isocyanate-reactive groups (usually polyol(s)), thereby to form a prepolymer bearing lateral carboxylic acid groups, followed by chain-extension with an active hydrogen containing compound (e.g. an alcohol, hydrazine or amine compound). Some of the carboxylic acid groups of the polyurethane may be neutralized with an appropriate base to render the polyurethane more readily water-dispersible. The polyurethane may also incorporate nonionic groups (such as polyoxyethylene groups) to render the polyurethane more water-dispersible (or a combination of both expedients could be used). The incorporation of such dispersing groups into a polyurethane is well known in the art and need not be discussed here in detail.

The water-dispersible polyurethane prepolymers may be used to form a aqueous dispersible polymer bearing cyclic carbonate groups and/or amine groups. For example, an isocyanate-terminated polyurethane prepolymer may be reacted with a hydroxy cyclic carbonate, such as glycerol carbonate, to form a polyurethane having one or more pendant cyclic carbonate functional groups. Amine functional groups may be introduced into a polyurethane polymer by reacting an isocyanate-containing prepolymer with an excess of a hydrazine and/or a polyamine, e.g. a diamine such as propylenediamine. Amine groups may also be introduced by reacting a carboxylic acid-containing polyurethane prepolymer with an aziridine compound to form a polymer having pendant aminoalkyl carboxylate groups.

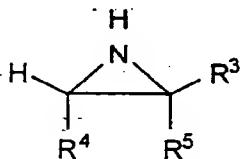
Hydroxy cyclic carbonate compounds may be employed to form a cyclic carbonate-functional ethylenically unsaturated monomer or to introduce a cyclic carbonate group into a polymer via reaction with an appropriately functionalized prepolymer. Hydroxyalkyl cyclic carbonate compounds are particularly useful in reactions of this type. Examples of suitable hydroxyalkyl cyclic carbonates include compounds having the formula:



where n is an integer from 1 to 6 and R^6 , R^7 and R^8 are independently chosen from hydrogen, alkyl, benzyl and aryl. A preferred cyclic carbonate for use in the preparation of cyclic carbonate-functional ethylenically unsaturated monomers and cyclic carbonate-functionalized polymers is glycerol carbonate (i.e., where n is 1 and R^5 , R^6 and R^7 are hydrogen).

In a preferred embodiment of the invention, the coating composition includes an aqueous dispersion of a polymer bearing both chain-pendant cyclic carbonate groups and chain-pendant amine groups. Functionalized polymers of this type may include a polyurethane backbone or be based on a vinyl addition polymer. The vinyl addition polymers may be prepared by reacting a monomer mixture which includes a cyclic carbonate-functional ethylenically unsaturated monomer and a carboxylate-functional ethylenically unsaturated monomer to form a first vinyl polymer. The reaction of the monomer mixture is typically carried out in the presence of a free radical polymerization initiator. Typically, the monomer mixture also includes an additional copolymerizable monomer.

The first vinyl polymer produced by the polymerization of the monomer mixture includes cyclic carbonate groups and carboxylate groups. At least a portion of the carboxylate groups on the first vinyl polymer may then be reacted with an aziridine compound to form a second vinyl polymer which includes aminoalkyl carboxylate groups. The aminoalkyl carboxylate groups formed by the reaction of the aziridine compound with carboxylate groups (which are defined to include salts of carboxylic acids for the purposes of this invention) to produce a polymer having an aminoalkyl carboxylate group of the formula $-C(O)-O-R^2-(NH-R^2)_m-NH_2$ where m is typically 0 to about 4 and R^2 is an ethylene or substituted ethylene group. Examples of suitable aziridine compounds which may be employed to introduce an amino group into a carboxylate-containing polymer include aziridine compounds described by the formula:



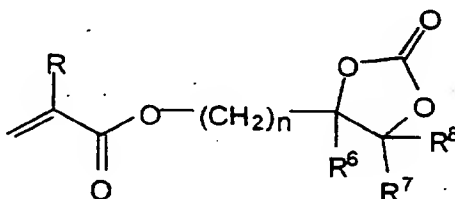
where R^3 and R^5 may be the same or different and are selected from hydrogen, benzyl, aryl and lower (C_1 - C_6) alkyl and R^4 is hydrogen or lower alkyl. Preferably, R^2 is ethylene (derived from ethyleneimine) or a methyl-substituted ethylene (derived from propyleneimine). Polymers bearing aminoalkyl carboxylate groups where R^2 is a methyl-substituted ethylene may be produced by the reaction of a carboxylic acid (or salt thereof) with propyleneimine.

In one embodiment of the invention, the functionalized vinyl addition polymer may be prepared by a process which includes the staged addition of different monomer mixtures. For example, in an initial stage the monomer feed may include a cyclic carbonate-functional ethylenically unsaturated monomer and a copolymerizable monomer together with a relatively small amount of a carboxylate-functional ethylenically unsaturated monomer. In a later stage, the monomer feed may be altered to include only one or more copolymerizable monomers and a larger percentage of carboxylate-functional ethylenically unsaturated monomer(s). As indicated herein, amine groups may then be introduced into the polymer by reaction of at least a portion of the carboxylate groups with an aziridine. This type of process may result in the production of a polymer which includes amine groups predominantly in a first region and cyclic carbonate groups predominantly in a second region.

The staged monomer feed process described supra may result in the formation of a vinyl addition polymer having a core/shell structure. For example, by controlling the timing and composition of the monomers introduced during various stages of the polymerization process, a polymer having cyclic carbonate groups primarily present in the core and amine groups primarily present in the shell may be produced. Similarly, by reversing the order of addition of the monomers it is possible to produce a polymer having amine groups primarily present in the core and cyclic carbonate groups primarily present in the shell.

Cyclic carbonate-functional ethylenically unsaturated monomers for use in preparing the present functionalized vinyl addition polymers may have a number of forms including carbonate-containing esters of (meth)acrylates, vinyl carbonates and monomers having a cyclic carbonate group linked to the unsaturated functional group through a urethane linkage. Cyclic carbonate-functional ethylenically unsaturated monomers may be formed from an epoxyalkyl ester of an α,β -unsaturated

monocarboxylic acid. The unsaturated epoxy ester may be converted to a cyclic carbonate ester by reaction of the epoxy group with carbon dioxide ("CO₂") in the presence of a catalyst, such as a triarylphosphine. By way of illustration, a glycidyl ester of acrylic acid or methacrylic acid can be reacted with CO₂ in the presence of triphenylphosphine to produce an acrylate or methacrylate ester of glycerol carbonate. Examples of suitable cyclic carbonate-functional ethylenically unsaturated monomers include substituted alkyl (meth)acrylate compounds of the formula:

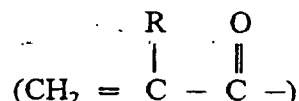


wherein R is H or methyl, n is an integer from 1 to 4, and R⁶, R⁷ and R⁸ are independently chosen from hydrogen, alkyl, benzyl and aryl. Preferably R⁶, R⁷ and R⁸ are hydrogen and n is 1.

A cyclic carbonate-functional ethylenically unsaturated monomer also may be prepared from an isocyanate compound having an ethylenically unsaturated group. The ethylenically unsaturated group may be a vinylaromatic group or a (meth)acryloyl group. While the isocyanate compound typically includes a single ethylenically unsaturated group, an isocyanate compound which includes two or more ethylenically unsaturated groups may also be employed. As used herein, the term "vinylaromatic group" includes groups having either an unsubstituted or substituted ethylene group attached to an aromatic ring. One example of a suitable vinylaromatic group is a vinylbenzene ("styryl") group. Examples of suitable isocyanate compounds having an ethylenically unsaturated group include α,α -dimethyl-m-isoprenyl benzyl isocyanate (m-TMI; available from Cytec, Stamford, CT), an isophorone diisocyanate/hydroxyethyl acrylate monoadduct ("IPDI/HEA"), an isophorone diisocyanate/ hydroxyethyl methacrylate monoadduct ("IPDI/HEMA"), isocyanatoethyl acrylate and isocyanatoethyl methacrylate. IPDI/HEA may be formed from a reaction mixture which includes isophorone diisocyanate and hydroxyethyl acrylate.

IPDI/HEMA may be formed from a reaction mixture which includes isophorone diisocyanate and hydroxyethyl methacrylate.

As used herein, the terms "(meth)acrylate," "(meth)acrylamide," and "(meth)acrylic" refer to functional groups which include a "(meth)acryloyl" moiety. For the purposes of this invention, the term "(meth)acryloyl" moiety is represented by the formula:



where R is H or a lower alkyl group (i.e., an alkyl group having one to six carbon atoms) and, preferably, R is H or CH₃. Thus, the term "(meth)acryloyl" includes both acryloyl (R = H) and methacryloyl (R = CH₃) moieties as well as a number of alkyl substituted analogs. The (meth)acryloyl moiety may be present as part of a carboxylic acid group, an ester group, e.g., an acryloyloxy group (CH₂=CHC(O)O-), or an amide group, e.g., an methacrylamido group (CH₂=C(CH₃)C(O)NH-). Preferred (meth)acryloyl groups include acryloyloxy and methacryloyloxy.

An ethylenically unsaturated isocyanate compound may be reacted with a hydroxyalkyl cyclic carbonate compound to form a difunctionalized urethane compound including ethylenically unsaturated group and a cyclic carbonate group. For example, a difunctionalized urethane compound may be prepared by reacting an unsaturated isocyanate, such as IPDI/HEMA or IPDI/HEA, with a hydroxyalkyl cyclic carbonate (e.g., glycerol carbonate). Another difunctionalized urethane compound may be prepared by reacting α,α -dimethyl-m-isoprenylbenzyl isocyanate (m-TMI) with glycerol carbonate to form a difunctionalized urethane compound which includes a cyclic carbonate group and a styrene moiety. The difunctionalized urethane compounds may be employed as a cyclic carbonate-functional ethylenically unsaturated monomer in the preparation of a vinyl addition polymer bearing chain-pendant cyclic carbonate groups.

Monomers which are suitable for use as a carboxylate-functional ethylenically unsaturated monomer in the preparation of polymers of the present invention include α,β -monoethylenically unsaturated carboxylic acids and salts thereof. α,β -Unsaturated mono- and dicarboxylic acids having 3 to 5 carbon atoms are particularly useful in preparing carboxylic acid-bearing vinyl addition polymers. Examples of suitable

carboxylate-functional ethylenically unsaturated monomers include fumaric acid, itaconic acid and (meth)acrylic acids, such as acrylic acid and methacrylic acid.

5 Examples of copolymerizable monomers which may be employed in the preparation of vinyl addition polymers include conjugated dienes (e.g., butadiene and isoprene), vinyl aromatic compounds (e.g., styrene and divinyl benzene), (meth)acrylate esters, vinyl halides, vinyl esters, vinyl ethers, heterocyclic vinyl compounds, vinylidene chloride, (meth)acrylamides, (meth)acrylo-nitriles (e.g., acrylonitrile) and alkyl esters of monoethylenically unsaturated dicarboxylic acids (e.g., di-n-butyl fumarate). Suitable (meth)acrylate esters which may be utilized as copolymerizable monomers include alkyl
10 (meth)acrylates, cycloalkyl (meth)acrylates (e.g., cyclohexyl acrylate) and alkyl (meth)acrylates, such as hydroxyethyl methacrylate ("HEMA") and hydroxyethyl acrylate ("HEA"). Styrene and lower alkyl (meth)acrylates, such as butyl acrylate and butyl methacrylate, are examples of preferred copolymerizable monomers which may be employed in the preparation of the present functionalized vinyl addition polymers. As
15 used herein, the term "lower alkyl" includes alkyl groups having from one to six carbon atoms. In this specification where an alkyl ester is employed, the use of a lower alkyl ester is typically preferred.

In other embodiments of the invention, the aqueous-based polymer system may not include both cyclic carbonate groups and amine groups in the same molecular entity.
20 For example, the present coating composition may include a polymer system in which the cyclic carbonate groups and the amine groups are present on separate polymer molecules. As with polymer systems having polymers bearing both types of functional groups in the same polymer, the functionalized polymers may include a polyurethane backbone or a vinyl addition polymer. Such polymers can be readily produced using the
25 general methods discussed herein. As such preparations are well known to those skilled in the art, the preparation of polymers bearing either the cyclic carbonate groups or the amine groups need not be discussed in further detail.

The coating composition may also include one or more of a group of ingredients which are collectively referred to as performance modifying additives. The composition
30 typically contains more than one performance-enhancing additive and may contain many such ingredients. Performance modifying additives such as a surface active agent, a light stabilizer, a ultra violet radiation (UV) absorber, a pigment, mixing or grinding

aids and/or a filler may be employed in the coating composition. Some characteristics of performance-enhancing additives and additional members of this category are described below.

5 The inclusion of a light stabilizer in the coating composition may lead to a coating having enhanced weathering characteristics. For example, coating compositions which include a hindered amine light stabilizer such as Tinuvin 440 or Tinuvin CGL 123 (available from Ciba Geigy Corporation) may be used to form coatings having excellent weathering properties.

10 A surface active agent which modifies the interaction between the coating composition and the substrate may be added to the composition. The inclusion of a surface active agent in the coating composition may modify the ability of the composition to wet a surface. In addition, the surface active agent may affect a number of properties of the coating composition, including how the coating composition is handled, how it spreads across the surface of the substrate, and how it bonds to the
15 substrate. Examples of suitable surface active agents include defoaming agents, flow agents, and the like. When present, the surface active agent typically makes up about 0.1 to about 1.5 wt.% of the non-volatile content of the coating composition.

20 Fillers or inert ingredients may advantageously be added to the coating composition. Fillers and inert ingredients include, for example, clay, glass beads, calcium carbonate, talc, silicas, organic fillers, synthetic polymer resins, and the like. Fillers extend, lower the cost of, alter the appearance of, and provide desirable characteristics to the composition before and after curing. Fillers or inert ingredients, when present, typically make up from about 5 to about 10 wt.% of the coating composition.

25 The invention may also include other ingredients which modify properties of the curable coating composition as it is stored, handled, or applied, and at other or subsequent stages. Waxes, pigments, gloss enhancing additives, gloss control additives, adhesion agents, and other performance-enhancing additives may be employed in this invention as required in amounts effective to upgrade the performance of the coating
30 composition and the cured coating. Desirable performance characteristics of the coating include chemical resistance, abrasion resistance, hardness, gloss, reflectivity, appearance, or combinations of these characteristics, and other similar characteristics.

Additives which provide such properties are also included in the invention. For some applications, a coating which is opaque, colored, pigmented, or has other visual characteristics may be desired. Suitable pigments which may be added to the coating composition include, for example, carbon black, cyanine blue, and titanium white.

5 The curable coating composition also optionally contains materials that give particular characteristics to the cured coating. For example, agents that modify the surface of the coating (surface-modifying agent) such that it is resistant to marring may be included in the composition. Agents may also be added to the coating composition to increase the hardness and/or abrasion-resistance of the coating.

10 The coating composition may be applied to a substrate by a variety of conventional methods. These methods include rolling, spreading, and spraying. The coating composition may be applied to the entire surface prior to curing. Alternatively, it may be applied in strips or areas, each of which is cured in succession. The present composition may be applied to a wide variety of substrates, including relatively rigid
15 substrates such as wood, metal, glass, and cement. A protective or decorative coating may also be formed on a flexible substrate such as a film, sheet metal, or cloth using the present coating composition.

The invention will be further described by reference to the following detailed examples. Parts and percentages, unless otherwise designated, are parts and percentages
20 by weight.

Example 1. Synthesis of Latex A

Monomer Feed No. 1

a)	DI H ₂ O	174.7
25 b)	Rhodafac RE-610 ¹	3.7
c)	KOH	.53
d)	Butyl Acrylate	175.0
e)	Styrene	101.4
f)	Butyl Methacrylate	100.9
30 g)	Acrylic Acid	6.3
h)	Methacrylic Acid	6.3
i)	Glycidyl Methacrylate Carbonate	50.0

Monomer Feed No. 2

j)	DI H ₂ O	74.9
k)	Rhodafac RE-610 ¹	1.58
l)	KOH	.23
m)	Styrene	43.5
n)	Butyl Methacrylate	113.4
o)	Acrylic Acid	15.8
p)	Methacrylic Acid	15.8

Procedure

Deionized water (420.0 g) and Rhodafac RE-610 (11.25 g; a nonylphenol 9-EO phosphate ester surfactant available from Rhone Poulenc, Cranbury, NJ) was charged to a three liter glass reaction flask equipped with a stirrer, condenser, nitrogen inlet, temperature probe, and addition inlet. A mixture of KOH (1.5 g), ammonium persulfate (1.35 g) and deionized water (40.0 g) was added with 10% (62 grams) of a pre-emulsion of components (a)-(i) (monomer feed No. 1) and the resulting mixture was heated to 86°C. A portion (70%) of a solution of ammonium persulfate (1.8 g) in 30 ml deionized water (22.3 g) was added to the remaining pre-emulsion of monomer feed No. 1, which was then added over a 70 minute period while the reaction mixture was maintained at 88-89°C. After the addition of monomer feed No. 1 was completed, the remainder (30%) of the aqueous ammonium persulfate solution (9.5 g) was added to a pre-emulsion of components (j)-(p) (monomer feed No. 2) which was then fed into the reaction mixture over a 40 minute period. Once the addition of monomer feed No. 2 was completed, the pump lines were washed with 74 ml deionized water and the reaction mixture was held for 1.5 hours at 88-89°C. The reaction mixture was then cooled to approximately 40°C and ammonia (11.6 g) was added. The resulting mixture was allowed to mix for 5 minutes. After heating the reaction mixture to 60°C, propylene imine (28.9 g) dissolved in deionized water (8.0 g) was added over 30 minutes. The resulting mixture was held for 1 hour at 60°C, then cooled and filtered. The final product had a solids content of 44.2 wt.% and a pH of 9.4.

Example 2. Synthesis of Carbonate Monomer I

A two liter round bottom flask was charged with 377.4 grams of isophorone diisocyanate (IPDI). The IPDI was heated to 45°C while a subsurface air sparge was introduced. The subsurface air sparge was then continued throughout the reaction. A mixture of 197.2 grams of 2-hydroxyethyl acrylate, 1.6 grams of MEHQ, and 0.8 grams of dibutyl tin dilaurate was then added in two hours while maintaining the reaction mixture at 40-45°C. The reaction mixture was then heated to 60°C and held at that temperature for 1 hour. After heating the reaction mixture to 70°C, a mixture of 200.6 grams of glycerol carbonate and 0.8 grams of BHT was added over 1.5 hours. The reaction mixture was then diluted slightly with 50 grams of 3-methoxypropyl acetate ("PM Acetate") and held at 70°C for 1.5 hours. An additional 88 grams of PM Acetate was added and the reaction was finished by holding the reaction mixture at 80-85°C for 1.5 hours.

Example 3. Synthesis of Latex B**Monomer Feed No. 3**

a)	DI H ₂ O	174.7
b)	Rhodafac RE-610	3.67
c)	KOH	.53
d)	Butyl Acrylate	175.0
e)	Styrene	101.4
f)	Butyl Methacrylate	100.9
g)	Acrylic Acid	6.3
h)	Methacrylic Acid	6.3
i)	Carbonate Monomer I Sol'n	58.8

Monomer Feed No. 4

j)	DI H ₂ O	74.9
k)	Rhodafac RE-610	1.58
l)	KOH	.23
m)	Styrene	43.5
n)	Butyl Methacrylate	113.4
o)	Acrylic Acid	15.8
p)	Methacrylic Acid	15.8

Procedure

Latex B was prepared according to the procedure described in Example 1 above except that monomer feed Nos. 3 and 4 were substituted for monomer feed Nos. 1 and 2 respectively. The resulting product had a solids content of 44.2 wt.% and a pH of 9.2.

Example 4. Synthesis of Comparison Latex C

Latex C was prepared according to the procedure described in Example 1 for the preparation of latex A except that the glycidyl methacrylate carbonate component in monomer feed No. 1 was replaced with methyl methacrylate. Latex C thus provided a comparison coating composition in which one of the functional groups (the cyclic carbonate groups) needed for crosslinking the latex was missing from the aqueous dispersion system.

Example 5. Film Properties of Lattices A, B and C

The latex compositions A and B described above were drawn down onto glass plates using a Bird bar which gave approximately one mil of dry film. The films were either allowed to dry for 24 hours at room temperature and the MEK solvent resistance was then tested or the films were cured at 160°F for 20 minutes and the MEK resistance was tested immediately after the film had cooled. As a control, comparison latex C was subjected to the testing protocol. This comparison permitted an assessment of the effect on film properties resulting from the removal of one of the functional groups (the cyclic carbonate groups) needed for crosslinking from the aqueous dispersion system.

The results are shown in Table 1 below. These results demonstrate that both lattices A and B had superior solvent resistance compared to the latex C indicating crosslinking had occurred in the films prepared from latex A and B and not in the case of latex C.

TABLE 1
FILM PROPERTIES OF LATTICES A, B AND C

	Latex A	Latex C (Comparison)	Latex B
Appearance	clear, no tack	clear, no tack	clear, no tack
MEK-double rubs; Film cured 24 hr. @ Room Temp.	200 +	80	250 +
MEK-double rubs; Film cured 20 min. @ 160°F	175		
MEK-double rubs; Latex stored 30 days @ 110°F, then formed into Film cured 24 hr. @ Room Temp.	200 +		

Soxhlet gel-sol extraction testing was carried out on the latex A and latex C.

5 The percent gel or amount of film which was not solubilized by the solvent (acetone) is a measure of crosslinking in this test since a truly crosslinked film would be insoluble. As a control, a commercial carboxylic acid functional latex (Neocryl A-601; available from Zeneca Resins, Wilmington, MA) was blended with a trifunctional aziridine crosslinking agent (CX-100; available from Zeneca Resins) in the ratio (Neocryl A-
10 601/CX-100) of 25.0/0.71. The Neocryl A-601/CX-100 system is considered by those skilled in the art to be an example of a latex system which produces a highly crosslinked latex film.

The lattices tested were drawn down on polyethylene sheets to give approximately one mil dry films. The films were air dried for one week at room
15 temperature. The films were pulled from the polyethylene sheets and placed in a Soxhlet extractor using acetone as the solvent. The extraction was run for 44 hours total with 24 hours at reflux and 20 hours with the films soaking at room temperature. The following results were obtained:

	<u>% Gel</u>
20 Latex A	91.0
Latex C	14.0
Neocryl A-601/CX-100	91.3

These results indicate that the cyclic carbonate/amine based latex system of the present invention (Latex A) provides a highly crosslinked latex after being cured at ambient temperature. The level of crosslinking observed with the present cyclic carbonate/amine based latex system is comparable to that observed with the Neocryl A-601/CX-100 system. In contrast, the comparison latex system lacking the cyclic carbonate functional groups (Latex C) shows a very low degree of crosslinking under ambient temperature cure conditions.

In addition, the data in Table 1 demonstrate that Latex A, which contains a vinyl addition polymer bearing both cyclic carbonate and amine functional groups had excellent storage stability. Even after storage for 30 days at an elevated temperature (110°F), Latex A retained its ability to be formed into a film and cured to form a coating having excellent solvent resistance (> 200 MEK-double rubs). In contrast, the commercial Neocryl A-601/CX-100 system must be sold as two-package system since the shelf life of compositions containing a carboxylic acid functional latex and multifunctional aziridine is extremely short, typically less than eight hours pot-life.

Example 6. Synthesis of Comparison Latex D

Monomer Feed No. 5

a)	Butyl Acrylate	306.6
b)	Methyl Methacrylate	310.0
c)	Methacrylic Acid	52.4
d)	Iso-butyl Methacrylate	116.8
e)	Glycidyl Methacrylate Carbonate	87.3

Procedure

Deionized water (915.2 g) and sodium laurel sulfate (64.0 g) were charged to a three liter glass reaction flask equipped with a stirrer, condenser, nitrogen inlet, temperature probe, and addition inlet. A mixture of NaHCO₃ (3.5 g), ammonium persulfate (4.36 g), and deionized water (100.0 g) was added to the flask with 8% (70 g) of monomer feed No. 5. The resulting mixture was heated to 85°C over approximately 55 minutes. The remainder of monomer feed No. 5 was added continuously over 2 hours and 10 minutes while maintaining the reaction temperature at 85°C. Once all of

monomer feed No. 5 was added, 40 grams of deionized water was added as a rinse. The reaction mixture was then maintained at 85°C for 55 minutes, followed by the addition of 0.5 grams of ammonium persulfate dissolved in 10 grams of deionized water. The resulting latex was held for another 45 minutes at 85°C. The reaction mixture was then cooled to room temperature and adjusted to a pH of 6.8 using ammonia.

Example 7. Synthesis of Comparison Latex E

Monomer Feed No. 6

a)	D1 H ₂ O	249.6
b)	Rhodafac RE-610	5.2
c)	KOH	0.75
d)	Butyl Acrylate	139.4
e)	Styrene	132.5
f)	Butyl Methacrylate	300.0
g)	Acrylic Acid	28.3
h)	Methacrylic Acid	28.3

Procedure

Deionized water (420.0 g) and Rhodafac RE-610 (11.25 g) were charged to the same glassware set-up as described in Example 6. A mixture of potassium hydroxide (1.5 g), ammonium persulfate (1.35 g), and deionized water (33.8 g) was added along with 10% (88 g) of monomer feed No. 6. The resulting mixture was heated to 87°C over approximately 55 minutes. A solution of 1.8 g of ammonium persulfate and 30 g of deionized water was added to the remainder of monomer feed No. 6. The resulting mixture was fed into the reaction flask over approximately 1 hour and 40 minutes. The temperature was allowed to slowly rise to 92°C during the addition. Once the addition of monomer feed No. 6 was completed, 74 g of deionized water was added as a rinse. The reaction mixture was then maintained at 92°C for 1 hour followed by the addition of 0.5 g of ammonium persulfate dissolved in 10 g of deionized water. The resulting latex was held for another hour at 90-91°C. The latex was then cooled to 48°C and adjusted to a pH of 6.0 with ammonia. The pH adjusted latex was heated to 60°C and a mixture of propylene imine (28.9 g) and deionized water (8.0 g) was added over 35

minutes, followed by the addition of 20 g of deionized water. The reaction was held for 1 hour at 60°C and then cooled. The final product had a solids content of 43.8 wt.% and a pH of 9.4.

Example 8. Preparation of Latex F

A dual polymer latex (Latex F) was prepared by blending together 30 g of Latex D and 30 g of Latex E to form an aqueous dispersion which contained a first polymer having pendant glycidyl carbonate ester groups and a second polymer having pendant amine groups. Latex F contained a 1:1 ratio of the first and second polymers on a weight basis. The ratio of cyclic carbonate to amine groups in Latex F was 1:1.5.

Example 9. Comparison of Film Properties of Lattices A, D, E and F

The latex compositions A, D, E and F described above were drawn down onto glass plates using a Bird bar which gave approximately one mil of dry film. The films were allowed to dry for 24 hours at room temperature then tested for MEK resistance using standard methods. This comparison provided one assessment of the effect on film properties resulting from the removal of one of the functional groups involved in the crosslinking reaction from the aqueous dispersion system. Latex D includes cyclic carbonate groups but no amine groups. Latex E includes amine groups but no cyclic carbonate groups. Latex A contains a polymer which includes both cyclic carbonate functional groups and amine functional groups. Latex F is a blend of Latex D (cyclic carbonate-containing polymer) and a second latex containing a polymer having pendant amine groups (Latex E).

Lattices A, D, E and F were also examined using the Soxhlet gel-sol extraction test described in Example 5 and a test for water resistance. The determination of water resistance was carried out on films prepared by drawing the latex compositions down onto leneta paper using a Bird bar to give approximately one mil of dry film. The resulting films were allowed to cure for three days at room temperature. A drop of water was then placed on each of the cured films. The water droplet was covered with a watch glass to prevent evaporation and the covered film was allowed to stand at room temperature for two and one half hours. The water was then removed by gently patting the film with a paper towel and the condition of the film which had been in contact with

the water droplet was observed. The condition of the film was rated using the following qualitative scale: 1 - totally dissolved; 2 - softened film (with whitening or blistering); 3 - somewhat softened film; 4 - slight film discoloration; 5 - no effect.

TABLE 2

FILM PROPERTIES OF LATTICES A, D, E AND F

	LATEX A	LATEX D	LATEX E	LATEX F
Soxhlet extract w/acetone (% gel)	91.0	-	68	56
Water Resistance	5	2 Soft film; whitening	2 Soft film; heavy blistering	5
MEK Resistance After Room Temp. 24 Hour Cure	200 +	15	150	130
Film Appearance	clear, no tack	light haze	clear, no tack	clear, no tack

The results are shown in Table 2. Lattices A, E and F could be cured to form clear, non-tacky films which had superior solvent resistance. The very low solvent resistance (15 MEK-double rubs) of Latex D, which included only pendant carboxylic acid and cyclic carbonate groups, indicates essentially no crosslinking occurred in the film formed from this latex.

The results of the Soxhlet gel-sol extraction tests of lattices E and F also suggested a high degree of crosslinking or interaction between the polymers in the film (compare the value for Latex A of 91% gel which is comparable to a commercial film considered to produce a highly crosslinked latex film).

The lack of water resistance of Latex E, however, indicates the solvent resistance and resistance to extraction by acetone are not the result of crosslinking but of an ionic interaction between the amine and carboxylic acid groups present on the polymers contained in the latex. In contrast, Latex F (which includes both a cyclic carbonate-

containing polymer and an amine-containing polymer) exhibits excellent water resistance in addition to solvent resistance and resistance to extraction by acetone. The water resistance of the film formed from Latex F indicates that the film is crosslinked and not merely held together by ionic interactions of amine and carboxylic acid groups.

5 The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

WE CLAIM:

1. An aqueous crosslinkable coating composition comprising an aqueous dispersion of (i) a first aqueous emulsion polymer including a plurality of cyclic carbonate groups and (ii) a second aqueous emulsion polymer including a plurality of amine groups or amine precursor groups.
2. The composition of claim 1 wherein the first and second aqueous emulsion polymers have a weight average molecular weight of at least about 100,000.
3. The composition of claim 1 wherein the second aqueous emulsion polymer includes a plurality of carboxylate groups and a plurality of aminoalkyl carboxylate ester groups.
4. The composition of claim 1 wherein the first aqueous emulsion polymer includes a plurality of five-membered ring cyclic carbonate groups; and the second aqueous emulsion polymer includes a plurality of $-C(O)-O-R^2-(NH-R^2)_n-NH_2$ groups, wherein n is 0 to about 4 and R^2 is $-CH_2CH_2-$ or $-CH(CH_3)CH_2-$.
5. An aqueous crosslinkable coating composition comprising a polymer having (i) cyclic carbonate groups and (ii) amine groups, amine precursor groups or a combination thereof.
6. The composition of claim 5 wherein the cyclic carbonate groups include a five-membered ring cyclic carbonate group or a six-membered ring cyclic carbonate group.
7. The composition of claim 5 wherein the polymer includes a primary amine group.
8. The composition of claim 5 wherein the amine group includes an aminoalkyl carboxylate group.

9. The composition of claim 8 wherein the aminoalkyl carboxylate group includes a group of the formula:

$-C(O)-O-R^2-(NH-R^2)_n-NH_2$, wherein n is 0 to about 4 and R^2 is ethylene or substituted ethylene.

10. The composition of claim 5 wherein the polymer includes an vinyl addition polymer formed from a process which includes:

- (i) reacting a monomer mixture including a cyclic carbonate-functional ethylenically unsaturated monomer and a carboxylate-functional ethylenically unsaturated monomer to form a first polymer which includes carboxylate groups; and
- (ii) reacting at least a portion of the carboxylate groups with an aziridine compound to form a second vinyl polymer including aminoalkyl carboxylate groups.

11. The composition of claim 10 wherein the carboxylate-functional ethylenically unsaturated monomer is acrylic acid, methacrylic acid or a mixture thereof.

12. The composition of claim 10 wherein the monomer mixture further includes a copolymerizable monomer.

13. The composition of claim 12 wherein the copolymerizable monomer is a conjugated diene, a vinyl aromatic compound, a (meth)acrylate ester, a vinyl halide, a vinyl ester, a vinyl ether, a heterocyclic vinyl compound, a (meth)acrylamide, a (meth)acrylonitrile, an alkyl ester of a monoethylenically unsaturated dicarboxylic acid or a mixture thereof.

14. The composition of claim 13 wherein the copolymerizable monomer is a lower alkyl acrylate, a lower alkyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, styrene, or a mixture thereof.

15. The composition of claim 5 wherein the polymer includes a core and a shell, wherein the core includes cyclic carbonate groups, and the shell includes amine groups.

16. The composition of claim 5 wherein the polymer includes about 0.1 to about 40 mole % polymerized units bearing amine groups or amine precursor groups, and about 0.1 to about 40 mole % polymerized units bearing cyclic carbonate groups.

17. The composition of claim 5 wherein the vinyl polymer includes an amount of amine groups within the range of about 1 to about 150 millimoles per 100 g of polymer solids and an amount of cyclic carbonate groups within the range of about 1 to about 150 millimoles per 100 g of polymer solids.

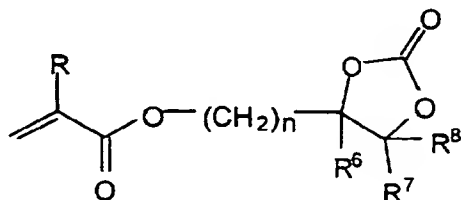
18. A polymer comprising (i) cyclic carbonate groups and (ii) amine groups, amine precursor groups or a combination thereof.

19. A method of preparing a polymer bearing cyclic carbonate groups and amine groups comprising:

- (i) reacting a monomer mixture which includes a cyclic carbonate-functional ethylenically unsaturated monomer and a carboxylate-functional ethylenically unsaturated monomer to form a first vinyl polymer including carboxylate groups; and
- (ii) reacting at least a portion of the carboxylate groups with an aziridine compound to form a second vinyl polymer including aminoalkyl carboxylate groups.

20. The method of claim 19 wherein the monomer mixture further comprises a copolymerizable monomer.

21. The method of claim 19 wherein the cyclic carbonate-functional ethylenically unsaturated monomer includes a substituted alkyl (meth)acrylate of the formula:



wherein R is H or methyl, n is an integer from 1 to 4, and R⁶, R⁷ and R⁸ are independently chosen from hydrogen, alkyl, benzyl and aryl.

22. The method of claim 19 wherein the cyclic carbonate-functional ethylenically unsaturated monomer includes a reaction product of a ethylenically unsaturated isocyanate monomer and a hydroxyalkyl cyclic carbonate.

23. The method of claim 22 wherein the ethylenically unsaturated isocyanate monomer includes a reaction product of a diisocyanate and a hydroxy-functional ethylenically unsaturated monomer.

23. A coated substrate formed by a process comprising:

(i) forming a film on a substrate from an aqueous crosslinkable coating composition which includes an aqueous dispersion of a polymer system having cyclic carbonate groups and amine groups or amine precursor groups; and

(ii) curing the film.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20735

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 8/32, 224/00; C08L 37/00
US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/507, 517, 549, 555; 523/201; 525/327.2, 329.9, 379; 526/269, 270, 314; 428/500

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; cyclic carbonate#, 1,3 dioxolan# 2 one, primary amine#, aziridine, emulsion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,431,791 A (DECEMBER et al) 11 July 1995, abstract, column 2, lines 39-51 and column 4, lines 24-28.	1-4, 23
X ---- Y	US 2,930,779 A (DRECHSEL) 29 March 1960, column 3, line 71 to column 4, line 48, column 6, line 69-75 and example 3.	23 ----- 5-7, 16, 18
X ---- Y	US 4,988,762 A (OVERBEEK et al) 29 January 1991, column 2, line 64 to column 3, line 18, column 4, lines 33-35 and examples 1-9.	1, 23 ----- 5-7, 16, 18
X ---- Y	US 5,374,699 A (IWAMURA et al) 20 December 1994, column 8, lines 4-10 and column 10, line 25 to column 11, line 11.	1, 23 ----- 5-7, 16, 18
X, P	US 5,567,527 A (WEBSTER et al) 22 October 1996, example 5.	1, 23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"I" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 MARCH 1997	Date of mailing of the international search report 10 APR 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TAE H. YOON Telephone No. (703) 308-2351

Form PCT/ISA 210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20735

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,569,715 A (GRANDHEE) 29 October 1996; column 6, lines 18-26 and 65, column 7, line 19 and column 8, lines 17-65.	1-23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20735

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

524/507, 517, 549, 555; 523/201; 525/327.2, 329.9, 379; 526/269, 270, 314; 428/500

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)